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by

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Vibrational Overtone Spectroscopy of π -Bonded Organometallic Complexes

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Abstract

The vibrational overtone spectra of gaseous butadiene iron tricarbonyl (BDIT), benzene chromium tricarbonyl (BCT), cycloheptatriene chromium tricarbonyl (CHTCT), and cyclooctatetraene iron tricarbonyl (COTIT) were recorded at the third overtone region using photoacoustic spectroscopy. These spectra were compared to the spectra of 1,3-butadiene, benzene, cycloheptatriene and cyclooctatetraene, respectively. The third overtone spectrum of BDIT shows three transitions corresponding to the three different C-H local mode oscillators, all shifted to the red compared to the corresponding peaks of 1,3-butadiene. No changes were observed in the overtone spectra of BCT and COTIT compared to the spectra of the corresponding hydrocarbon ligands. However, the third overtone spectrum of CHTCT contains two additional peaks. The presence of these additional transitions suggested vibrational coupling of the C-H stretch with other motions of the hydrocarbon ring bonded to the transition metal.

Introduction

Organometallic complexes are known for their catalytic activity in many chemical processes¹. The changes in the ligand properties during coordination accounts for the catalytic activity. Changes in the vibrational spectra of these complexes and the uncomplexed ligands have been studied in the IR and near-IR regions. Often these changes in the infrared spectrum are difficult to analyze because they must be considered in terms of normal modes. Although a normal coordinate analysis and vibrational assignments of the ligand may be available, this is usually not the case for the complexes. In this report we demonstrate the usefulness of vibrational overtone spectroscopy for tracking the effects of complexation on specific bonds within π -bonded organic ligands. Four ligand complex pairs have been selected: butadiene and butadiene iron tricarbonyl (BDIT); benzene and benzene chromium tricarbonyl (BCT), cycloheptatriene and cycloheptatriene chromium tricarbonyl (CHTCT); and cyclooctatetraene and cyclooctatetraene iron tricarbonyl (COTIT). Each of these ligands are π -bonded to their

respective metals in the complex. The high vibrational overtone spectrum of the ligands distinguishes the olefinic and methylenic C-H stretch absorptions uniquely. Shifts in the absorptions or the observation of new peaks reports on the changes which have occurred in the ligand during complexation.

The infrared spectra of 1,3 - butadiene and BDIT have been recorded.² Transitions in the C-H stretch region of neat liquid BDIT shift 42-65 cm⁻¹ to the red compared to the corresponding transitions for 1,3-butadiene. Davidson³ studied the IR and Raman spectra of liquid BDIT and assigned four transitions to the C-H stretch (3063, 3042, 3002, 2934 cm⁻¹), two peaks to the C-C stretch (1477 and 1439 cm⁻¹), and four C-H bends (1499, 1370, 1174, 1060 cm⁻¹). The infrared⁴ and overtone⁵ spectrum of benzene is well known and Lewis⁶ recorded the C-H stretch fundamental (3090 cm⁻¹), first overtone (6090 cm⁻¹) and several combination bands in the region between these C-H transitions in BCT using photoacoustic spectroscopy. The complex possessed three new bands compared to free benzene (4464, 4264 and 3953 cm⁻¹) which were assigned to combinations of the C-H stretch and other ring motions. The IR spectrum of CHTCT was recorded by Abel and colleagues⁷ and Gabelein⁸ who concentrated on the carbonyl stretch region and low energy IR vibrations of the complex. The IR spectrum of cycloheptatriene was also recorded⁹ and three transitions (3060, 3027, 3015 cm⁻¹) were identified in the C-H stretch region. Bailey et al.¹⁰ recorded the IR spectrum of COTIT and assigned three transitions (3075, 3040 and 3022 cm⁻¹) to the C-H stretch. Compared to the IR spectrum of cyclooctatetraene¹¹ (3013, 3015 cm⁻¹ C-H stretch; normal coordinate analysis) these transitions are shifted to the blue by 60, 25 and 7 cm⁻¹, respectively.

Most of the assignments discussed above fall at or below the first C-H overtone where many combination transitions are observed. These combination bands are difficult to identify because they usually overlap one another and there are many possibilities to select from. Overtone spectra above the first overtone yield more quickly to interpretation in the local mode picture where individual peaks are observed for each nonequivalent C-H bond in the molecule. A few reports of vibrational overtone spectra of organometallics have been published. Blackburn, Snavely and Oref¹² recorded the third C-H overtone spectrum of gaseous ferrocene extending

the work of Lewis⁶ who recorded the fundamental (3080 cm^{-1}) and first C-H overtone (6105 cm^{-1}) transitions for ferrocene in addition to five combination bands below 5000 cm^{-1} . Because the cyclopentadienyl ligand is aromatic in the complex the overtone spectrum could be expected to display only one peak at each overtone level. A comparison of the spectrum of cyclopentadiene to those of ferrocene, ruthenocene and related compounds in the third overtone region indicated that the peak attributed to the C-H olefinic stretch in cyclopentadiene split into four peaks in the complex. This observation was interpreted as coupling of the C-H stretch to other vibrations.¹³

Experiment.

The gaseous overtone spectra of organometallic complexes were obtained by using intracavity laser photoacoustic spectroscopy. The sample was vacuum-transferred into a 20 by 1.5 cm photoacoustic cell equipped with a 1751XA^{II} Qualitone microphone and Brewster's angle quartz windows. To increase the signal-to-noise ratio, argon was added to the photoacoustic cell to obtain a total pressure of approximately 500 torr. A specially designed intracavity oven heated the sample up to $120\text{ }^{\circ}\text{C}$. The temperature was controlled by the Omega Engineering, Inc. iron-constantan thermocouple.

Spectra-Physics series 2000 argon ion laser pumped Spectra-Physics Model 3900S CW Ti:Sapphire laser outfitted with the three-plate birefringent filter (2 cm^{-1} bandwidth). An Oriel Motor Mike with the 18007 control unit controlled the birefringent filter rotation. A McPherson Model 270 0.35 meter scanning monochromator with McPherson Model 789A scan control unit was used to measure the initial and final wavelengths of the scanning region. Because the resolution of monochromator is 0.3 cm^{-1} the measurements were limited by the 2 cm^{-1} resolution of the birefringent filter.

The PTI Model 03-OC4000 optical chopper chopped the argon laser beam at 250 Hz, providing the reference signal for an EG&G Brookdeal Electronics Model 5207 lock-in amplifier. An IBM computer was connected with both the lock-in amplifier and Oriel Motor Mike and recorded the photoacoustic signal controlling the wavelength scan.

The positions of the peaks were corrected using calibration procedure. It was discovered that the mechanical shift of the motor mike does not have a linear dependence from the wavelength. Therefore, the real wavelength values measured after each 500 μm of the micrometer scan and the peak positions were corrected according to these measurements.

Results and Discussion

The vibrational overtone spectra of 1,3-butadiene and BDIT at the third overtone region are shown in Figure 1. Three peaks assigned to the three different C-H oscillators¹⁴ appear in the spectra of both hydrocarbon ligand and complex. The metal complex transitions are shifted to the red compared to those of 1,3-butadiene indicating that the C-H bonds become longer when 1,3-butadiene is bonded to the metal. The lower energy peak is shifted by 57 cm^{-1} and two high energy peaks are shifted by 96 and 99 cm^{-1} (Table 1). The changes in the bondlength were estimated using the correlation given by Gough and Henry¹⁵:

$$r_{\text{final}} = r_{\text{initial}} - (\Delta\nu / 11v) * 0.001 \quad \text{or} \quad \Delta r = (\Delta\nu / 11v) * 0.001$$

where $\Delta\nu$ is the frequency shift and v is the vibrational quantum number. This equation was developed to estimate the bondlength of the halogen substituted benzenes compared to the benzene. We believe it is possible to use this correlation for conjugated π -bonded organometallic ligands. The estimated changes in the bond length for the C-H central bond, the C-H terminal bond *cis* to the central bond and the C-H terminal bond *trans* to the central bond are 0.0013 Å, 0.0022 Å and 0.0023 Å, respectively. Decrease in the π -bond strength upon coordination to the metal would lead to the observed changes in the C-H bond length for 1,3-butadiene.

The third overtone vibrational spectra of benzene⁵ and BCT are shown in Figure 2. The spectrum of the complex is similar to that of benzene. The transition energy and width for benzene are 11498 cm^{-1} (FWHM 82 cm^{-1}) and those for BCT are 11499 cm^{-1} (FWHM 98 cm^{-1}). From the overtone spectrum there is no evidence that the C-H bonds in the benzene ligand are different from free benzene. This in turn indicates no bond length changes in the C-C bonds.

The spectra of cycloheptatriene and CHTCT are shown in Figure 3. The spectrum of CHTCT is different from that of the hydrocarbon ligand. New transitions appear at 10932 cm^{-1}

and 11488 cm^{-1} and the most intense transition shifts 17 cm^{-1} to the red (Table 1). We believe that changes in the overtone spectrum of the complex arise from the vibrational splitting due to the coupling of the C-H stretch with the other motions of the cycloheptatriene ring.

The results for cyclooctatetraene and COTIT are shown in Figure 4. The overtone spectra of cyclooctatetraene and COTIT are very similar. The transitions for cyclooctatetraene and COTIT occur at 11284 and 11277 cm^{-1} and peak widths are 52 and 58 cm^{-1} , respectively. Although shifts to the blue were observed in the IR spectra of COTIT compared to that of cyclooctatetraene^{10,11}, none were evident in the overtone experiment. The infrared spectra of COTIT and cyclooctatetraene must be analyzed in terms of the different normal modes of vibration for the two separate molecules. The overtone spectra, however, report directly on the ligand vibrations, specifically the C-H stretches. Because we do not observe any changes in the overtone spectra of complex and ligand, the shifts observed in the infrared spectrum are probably the result of changes in the normal modes of vibration between the ligand and complex. In this case the overtone spectrum indicates that the metal does not change the C-H bond lengths of the cyclooctatetraene ring.

A combination of valence bond theory and concepts of aromaticity of the ligand aid in an explanation of these current results and also incorporates the observations for the metallocenes. Four peaks were observed for ferrocene, ruthenocene, acetylferrocene and cyclopentadienyl titanium trichloride in the region where the olefinic C-H stretch absorbs in cyclopentadiene¹³. All these compounds have their valence shells filled with electrons (see Figure 5) and, in each case, the cyclopentadiene ring becomes aromatic through complexation to the metal. The changes associated with becoming aromatic produce the observed vibrational spectrum. As a check of this explanation we recorded the vibrational overtone spectrum of chromocene in the same spectral region as the other metallocenes. Chromocene which has two unpaired electrons in the valence shells, lacks the stable electronic structure of the other metallocenes. Unlike the other metallocenes, the third overtone spectrum of chromocene (Figure 6) has only one peak (11632 cm^{-1}) which appears at the same transition energy as the olefinic C-H stretching absorption in cyclopentadiene (11652 cm^{-1})¹³. This result supports our argument that the complete electronic structure of the complex assists the vibrational coupling in organometallics.

The electronic diagrams in Figure 7 indicate that BDIT and COTIT have all their valence shells filled. The hydrocarbon ligands can be thought to donate electrons to the complexation bonds. However, in doing so they do not become aromatic as in the case of ferrocene. Their electronic configuration undergoes small changes relative to the free ligand and consequently no new peaks are observed in the overtone spectra. In BDIT red shifts of the peaks were observed indicating a lengthening of the CH bonds as discussed above. In the case of the BCT complex, the electronic structure is complete and benzene, being already aromatic, resists any structural changes. This leaves the spectrum of the complex unchanged. The cycloheptatriene ring, however, which possesses the perturbed boat conformation⁹ undergoes conformational changes when bonding to the metal. The degree of delocalization of the π -orbitals increases which planarizes the ring. These structural changes cause additional peaks to appear in the overtone spectrum.

Conclusions

The vibrational overtone spectra of gaseous butadiene iron tricarbonyl, benzene chromium tricarbonyl, cycloheptatriene chromium tricarbonyl and cyclooctatetraene iron tricarbonyl were recorded at the third overtone region and compared to the spectra of the corresponding hydrocarbon ligands. The results were different for each ligand-complex pair. For BDIT red shifts for all transitions were observed compared to the spectrum of 1,3-butadiene indicating an increase of the C-H bondlength in the complex. In case of BCT and COTIT overtone spectra of complexes were the same as the ligand spectra. The spectrum of CHTCT was different from the spectrum of cycloheptatriene. Two additional absorptions appeared in the spectrum of the CHTCT complex. These peaks were discussed in terms of vibrational coupling of the C-H stretch with other vibrations of the hydrocarbon ring. Two conditions in the complex electronic structure and aromaticity of the hydrocarbon ligand are necessary for these spectral changes. First, the electronic structure of the complex should be complete with all valence shells filled with electrons. Second, the ligand π electrons should become more delocalized when bonding to the transition metal.

Table 1. Third Overtone Spectra of Organometallic Complexes and Hydrocarbon Ligands.

Name of Compound	Peak positions, cm^{-1}	
1,3-butadiene	11339 11451 11550	11342* 11448* 11558*
butadiene iron tricarbonyl		11282 11355 11451
cyclopentadiene		11652**
chromocene		11632
benzene		11498***
benzene chromium tricarbonyl		11416 11499
cycloheptatriene		11094 11216 11366
cycloheptatriene chromium tricarbonyl		10932 11089 11349 11488
cyclooctatetraene		11284
cyclooctatetraene iron tricarbonyl		11277

* - values are taken from Ref. 14.

** - values are taken from Ref. 13.

*** - values are taken from Ref. 5.

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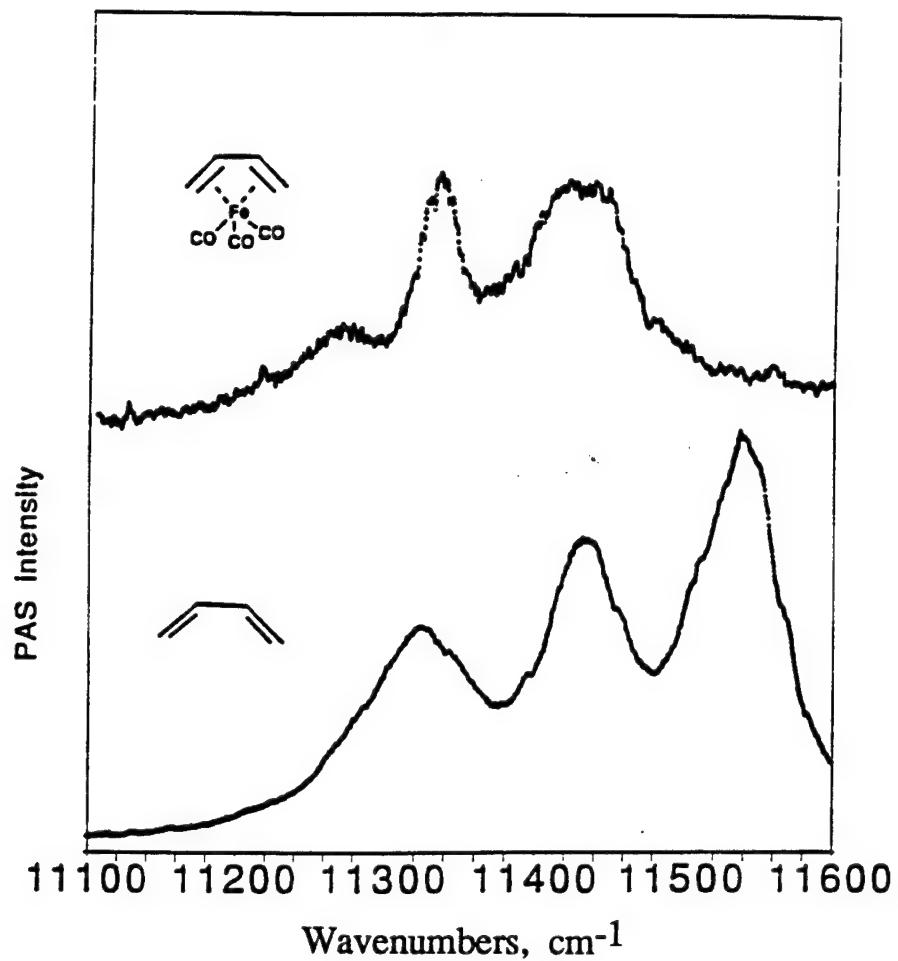


Figure 1. The third overtone spectra of 1,3-butadiene and butadiene iron tricarbonyl.

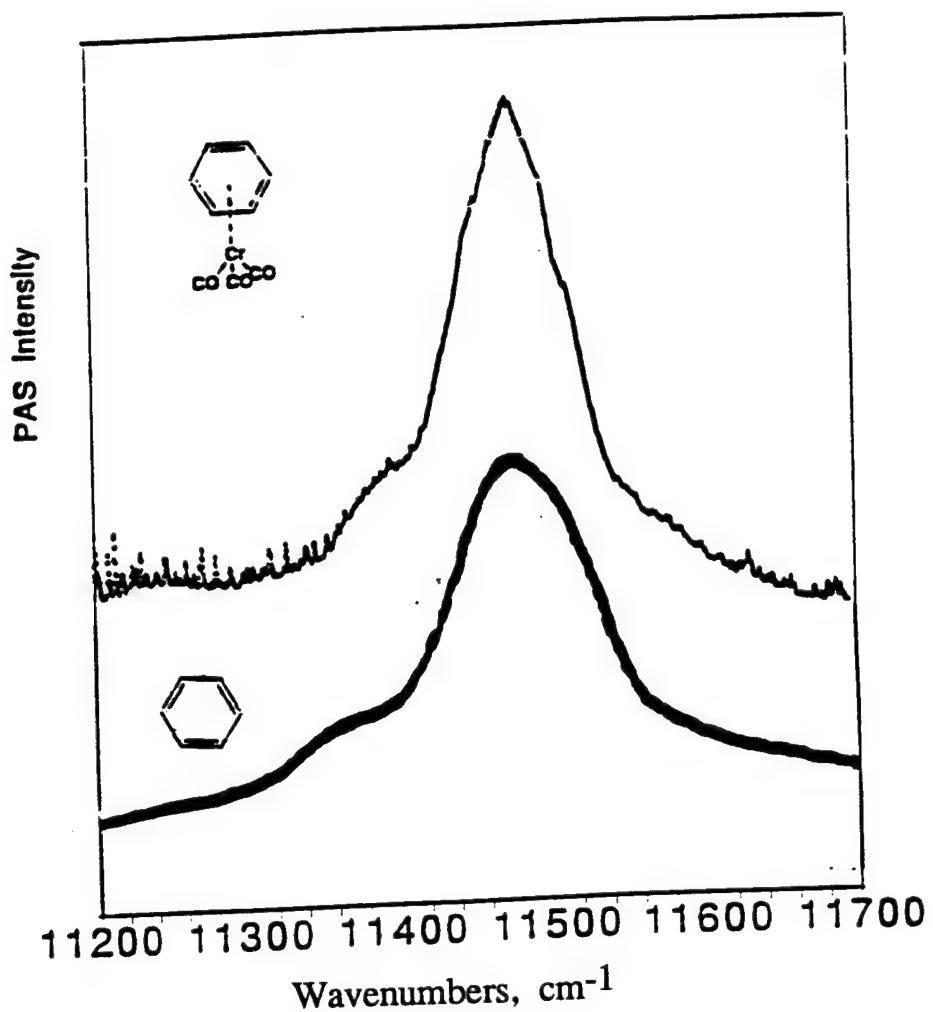


Figure 2. The third overtone spectra of benzene (taken from reference 5) and benzene chromium tricarbonyl.

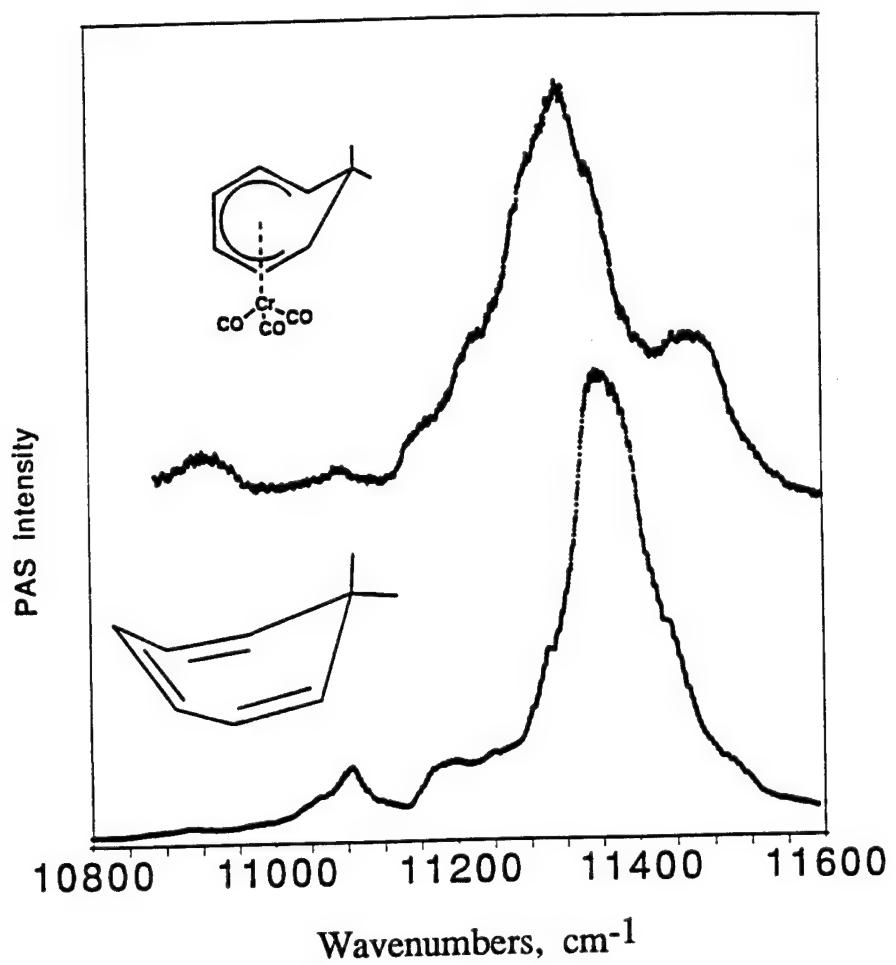


Figure 3. The third overtone spectra of cycloheptatriene and cycloheptatriene chromium tricarbonyl.

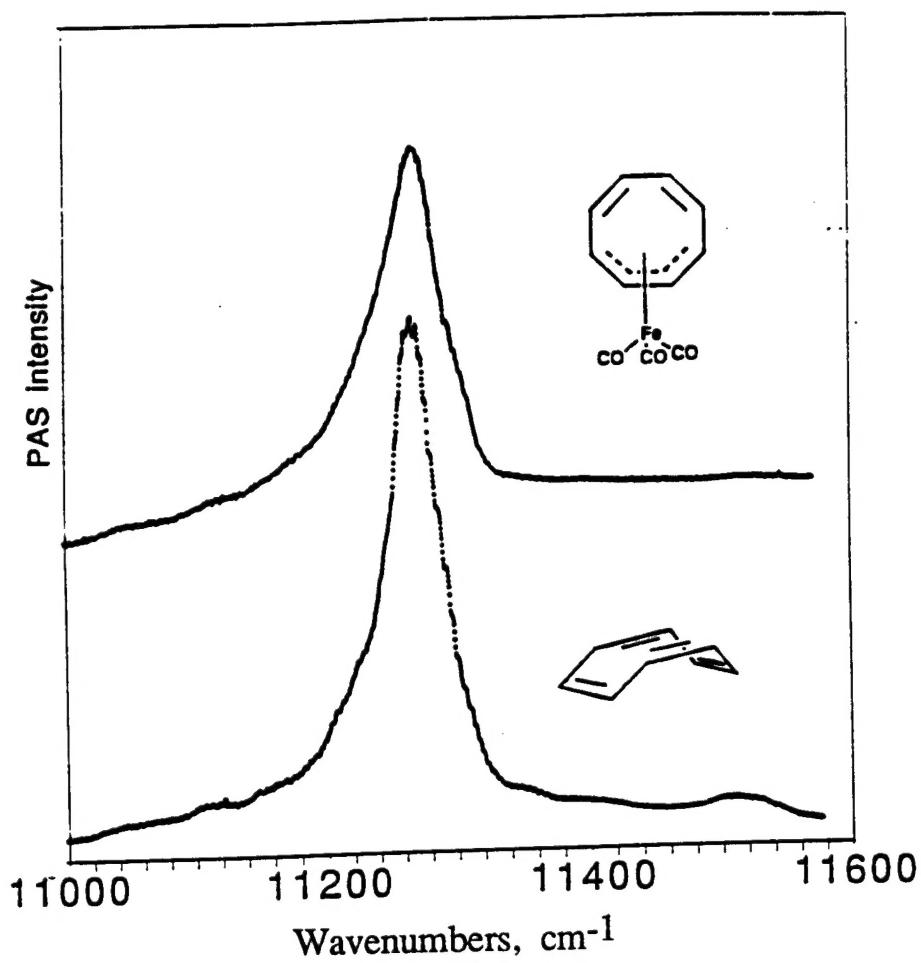


Figure 4. The third overtone spectra of cyclooctatetraene and cyclooctatetraeneiron tricarbonyl.

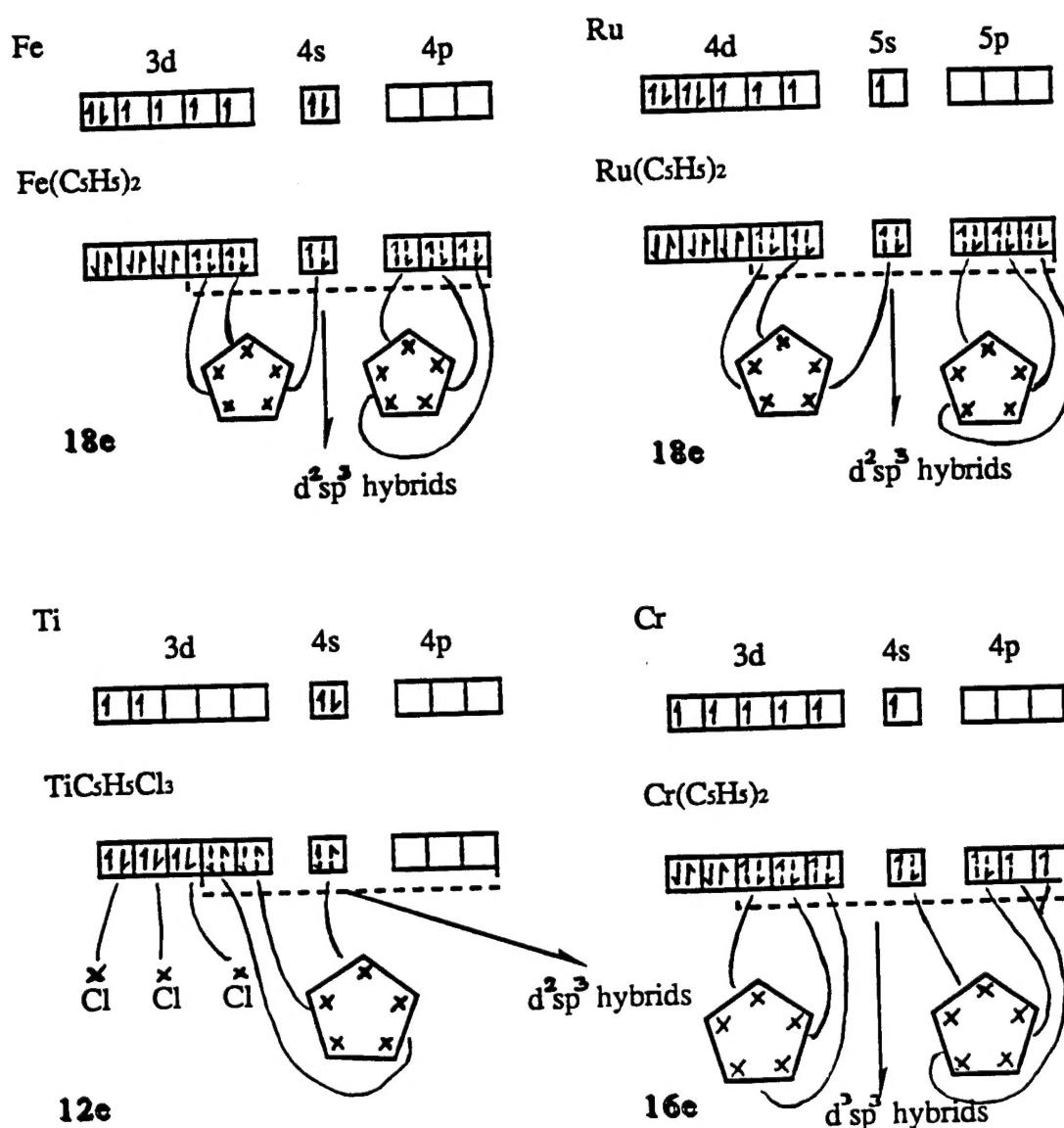


Figure 5. The Valence Bond Theory representation of bonding in metallocenes.

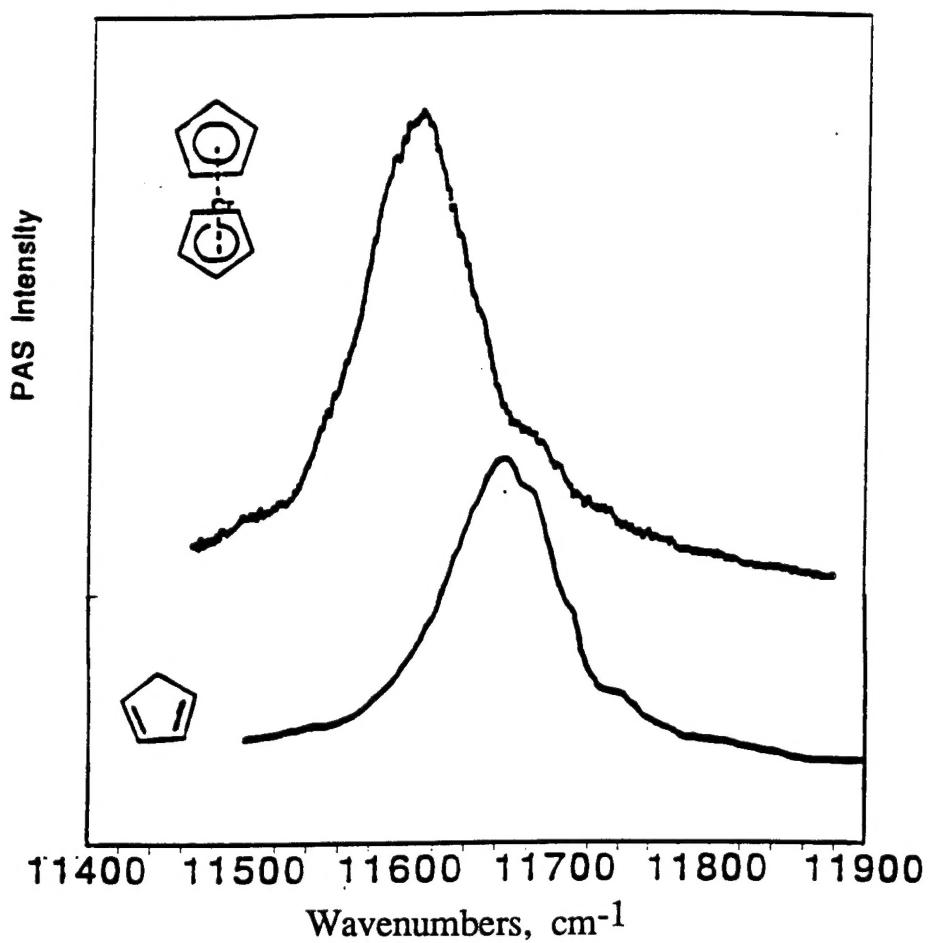
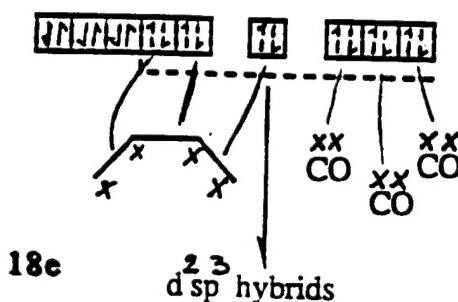
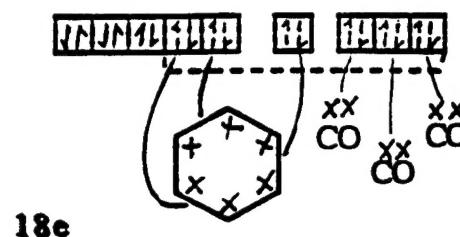


Figure 6. The third overtone spectra of cyclopentadiene (taken from Ref.13) and chromocene.

Fe



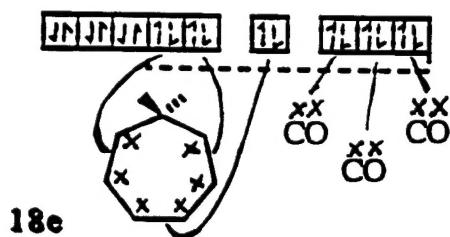
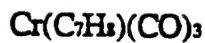
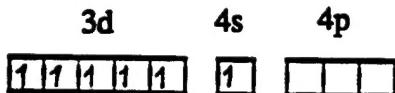
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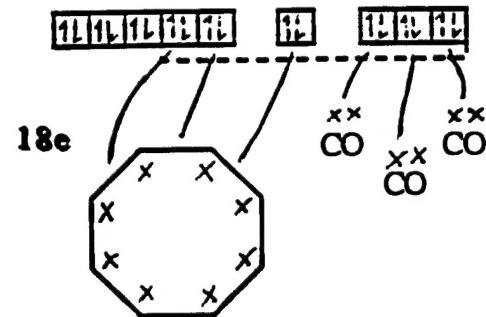
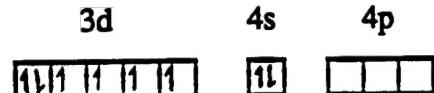


Figure 7. The Valence Bond Theory representation of bonding in the organometallic complexes.